

Study Optical and Electrical Properties of Cd_{1-x}Zn_xS Thin Films prepared by Spray Pyrolysis Technique

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Abstract— Nano particles of mixed Cd_{1-x}Zn_xS thin films were prepared by spray pyrolysis technique at a substrate temperature of 360°C. The films deposited were 160 nm thickness. Optical and electrical measurements such as, absorbance, absorption coefficient, optical energy gap, refractive index, Hall effect and D.C conductivity for all films we are measured. The results showed that absorbance of prepared films decreases with increasing of ZnS Vol % this lead to increase the energy gap. Conductivity decreased with increasing of ZnS Vol.%, as well as the results showed throughout the study that all films have low activation energy, its value increase with increasing of Vol.% of (x). Hall effect measurement showed all films has p-type Conductivity

Index Terms— Spray pyrolysis, cadmium sulphide, zinc sulphide, Absorbance, Optical Energy Gap, activation energy, Hall effect, D.C conductivity

I. INTRODUCTION

The group II–VI compound semiconductors have attracted considerable attention in both fundamental research and technological applications because of their wide use in the fabrication of solar cells and other optoelectronic devices [1]. Cd_{1-x}Zn_xS is a prominent ternary alloy among II–VI compound semiconductors for the fabrication of multilayer p–n junction's device without mismatch of lattice parameter and electron affinities. CdS is an p-type direct band gap semiconductor material and is extensively used as a window layer for the fabrication of solar cells [2]. However, due to its low band gap, CdS window layer absorbs the blue portion of the solar spectrum which causes a decrease in the current density of solar cells. For the high performance of a solar cell device, it is necessary to use an appropriate window material. Since Cd_{1-x}Zn_xS has a larger band gap than CdS, therefore the replacement of CdS with Cd_{1-x}Zn_xS film can lead to a decrease in window absorption losses, and has resulted in an increase in short-circuit current [3-5]. CdS and ZnS have a high melting point and good transmission, and does not easily react with oxygen and water vapor in the air, so it have high specific volume and good cycling performance. In addition, CdS and ZnS thin films are also used for film resistors, electric conversion films, heat reflective mirrors, semiconductor–insulator–semiconductor (SIS) heterojunction structures, and surface protection layers of glass.

The techniques which have been adapted for the preparation of Cd_{1-x}Zn_xS thin film of uniform composition are vacuum thermal evaporation [6], Chemical bath deposition [7], solution growth technique (SGT) [8], Spray Pyrolysis Technique [9], Screen printing and sintering [10] and vacuum

thermal evaporation [11] etc. In attempts to improvise the properties of CdS, it is being tried out to mix with other Sulphides.

II. MATERIALS AND METHODS

A spray pyrolysis techniques experimental setup was employed to prepare Cd_{1-x}Zn_xS mixed thin films on glass substrates (3×1.5×0.1 cm³) at a substrate temperature of 360 °C. The difference in ZnS Vol.% (x) was achieved by mixing the aqueous solutions of 0.1 M of cadmium and zinc acetates and thiourea to pre-determined volume ratio. The value of (x) in the solution was varied from 0 to 1 (x=0, 0.2, 0.4, 0.6, 0.8, 1). The mixed solutions which were then diluted with water formed the final spray solution and a total volume of 25 ml was used in each deposition. The deposition parameters such as spray distance between nozzle and substrate is (30 cm), spray time (4 s) and the spray interval (1 min) were kept constant. The carrier gas (filtered compressed air) flow rate was maintained at 6 l/min at a pressure of 6.5×10⁴ Nm⁻².

III. RESULTS AND DISCUSSION

1-Optical properties

The absorption spectra of the mixed Cd_{1-x}Zn_xS films recorded in the wavelength from 300 to 1100 nm are compared with Vol.% (x) in Figure (1). It was found that the absorbance decreases with increasing wavelength for all the prepared thin films. This physically means that a incident photon was not able to excite the electron and transfer it from valence band to the conduction band because the energy of incident photon less than the value of the energy gap value of the semiconductor this lead to the absorbance decrease with increasing of wavelength. It is also noticeable that the absorbance decreases with increasing Vol.% (x), this confirms Zinc atoms entry within the crystal structure of the prepared film, configure localized levels within the energy gap led to the absorption of photons with a low energies. Absorption spectra optical depend on the chemical composition, crystal structure, energy of the incident photon film thickness, and film surface morphology.

absorption coefficient (α) for the prepared thin films was calculated from equation [2]:

$$\alpha = \frac{2.303 \times A}{t} \quad \text{..... (1)}$$

t: is the thickness of thin film in (cm)., A: absorbation.

The values of α for all thin films are found to be greater than 10⁴ cm⁻¹ in the visible region, which means that the films have a direct optical energy gap [12]. The variation of the absorption coefficient (α) of Cd_{1-x}Zn_xS thin films is shown in Figure (2) as a function of wavelength, α decreases

with the increasing of wavelength and it is observed that the absorption coefficient α decreases with the increasing of the concentration of ZnS. This is due to the increasing of energy gap with a concentration of ZnS [13]. The values of absorption coefficient are in agreement with [14].

The optical energy gap of the most important constants in semiconductor physics, as it depends on the value of this constant use in the semiconductor optical and electronic applications [14]. A direct optical energy gap (E_g) was calculated by using the relation (2) with $r=1/2$ for the allowed direct transition, and from the Figure (3), the values of E_g were determined from the intersection point of the extrapolation of a linear curve with $h\nu$ axis.

$$\alpha h\nu = B (h\nu - E_g^{\text{opt}})^r \quad \dots\dots\dots (2)$$

Where: E_g^{opt} : energy gap between direct transition.

B: constant depended on type of material.

r: exponential constant, its value depended on type of transition,

From Figure(3.a), for $x = 1$ (CdS_{pure}) the energy gap equal 2.61 eV, it increases with decreasing CdS Vol.% to (2.9, 3, 3.13 and 3.35) eV at $x = 0.8, 0.6, 0.4$ and 0.2 respectively. As shown in Figure(3.b to e), Figure(3.f) represents the optical energy gap of the film (ZnS_{pure}) which equal 3.42 eV as shown in table (1).

This increasing is due to the decreasing of the density of state inside the optical gap, the increasing concentration of ZnS leads to decrease from the secondary levels and structure defects, which lead expand in the optical energy gap. The observed optical energy gap of CdS is compatible with the earlier reports [15]. The increase in value of optical energy gap here is important because it not easily the transmission of electrons from the valence to the conduction band which contributes to the use of these films in various electronic applications.

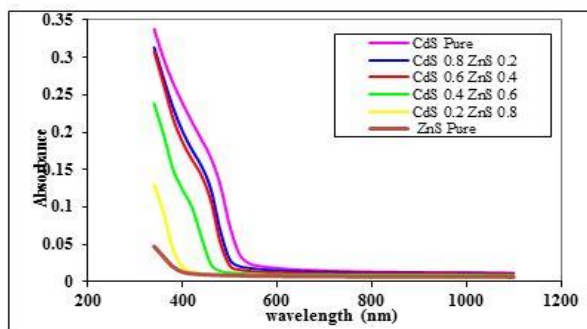


Figure (1): Absorbance as a function of wavelength for Cd_{1-x}Zn_xS films at different Vol.% of (x).

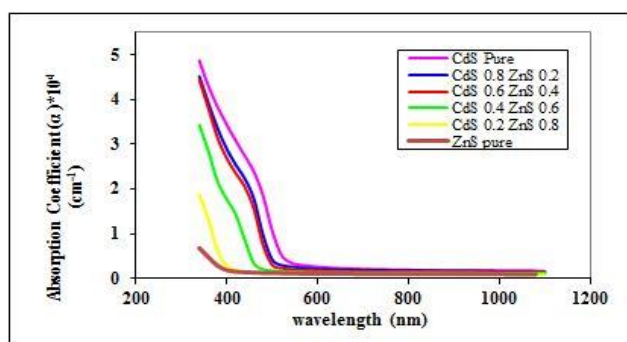


Figure (2): Absorption coefficients as a function of wavelength for Cd_{1-x}Zn_xS films at different Vol.% of (x).

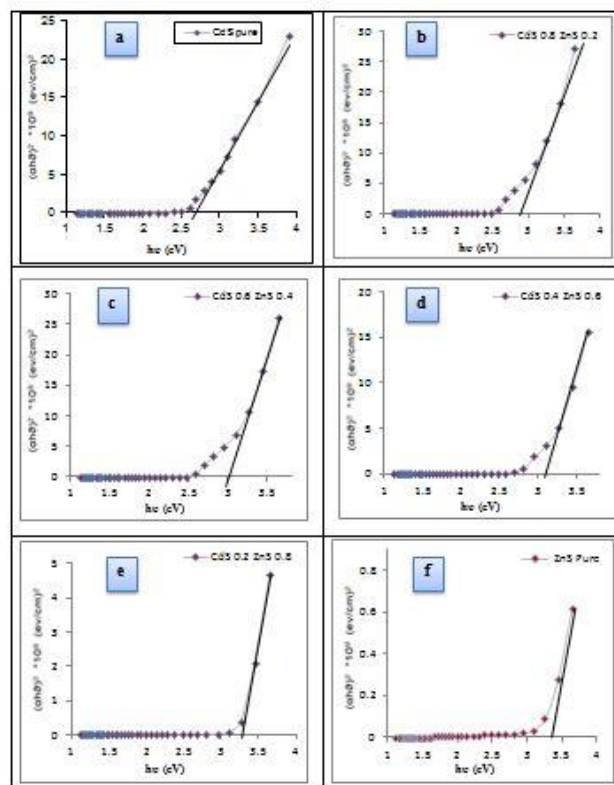


Figure (3): $(\alpha h\nu)^2$ as a function of $h\nu$ for Cd_{1-x}Zn_xS films at different Vol.% of (x).

Table 1: The values of optical energy gap for Cd_{1-x}Zn_xS thin films at different Vol.% of (x).

Sample	E_g (eV)
CdS _{pure}	2.61
CdS _{0.8} ZnS _{0.2}	2.92
CdS _{0.6} ZnS _{0.4}	3
CdS _{0.4} ZnS _{0.6}	3.13
CdS _{0.2} ZnS _{0.8}	3.35
ZnS _{pure}	3.42

The refractive index is the ratio between the speed of light in vacuum to its speed in material which doesn't absorb this light. The refractive index (n) was calculated from the following relation[2].

$$n = \left[\left(\frac{1+R}{1-R} \right)^2 - (K_0^2 + 1) \right]^{\frac{1}{2}} + \frac{1+R}{1-R} \quad \dots (4)$$

R: is reflectance.

The values of n vs. λ is shown in Figure (4). From those Figure the maximum value of n for all thin films is approximately equal to a value of 2.5. From Figure (4), n value decreasing with increasing λ , the explanation of this behavior may be related to the polarization of thin film because n depends on material polarization where with increasing polarization the velocity of light was decreased so n changed. The polarization depends on the crystalline and on the grain size of thin film so these depend on preparation conditions.

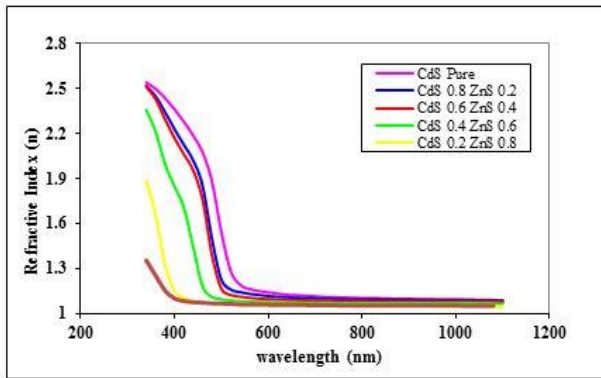


Figure (4): n as a function of wavelength for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films at different Vol.% of (x).

2-Electrical properties

The electrical conductivity has been measured as a function of temperature for films in the range (R.T – 200) °C by using the electrical circuit. The measurements have been done using sensitive digital electrometer type Keithley (2400) and electrical oven as show in Figure(5).

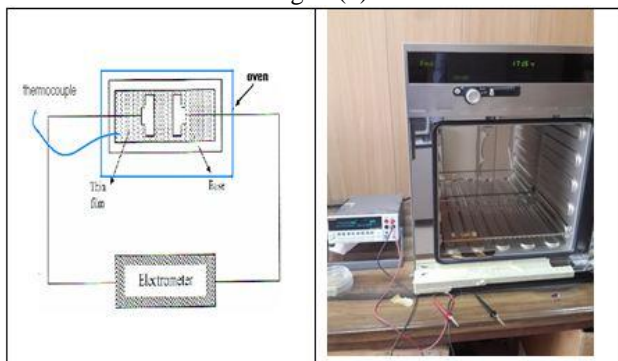


Figure (5): set-up and photograph illustrates the D.C electrical conductivity.

The resistivity (ρ) of the films is calculated by using the following equation:

$$\rho = \frac{R \times A}{L} \quad \text{..... (5)}$$

Where: R is the sample resistance.

A is the cross section area of the films.

L is the distance between the electrodes.

The conductivity of the films was determined from the relation:

$$\sigma_{D.C} = \frac{1}{\rho} \quad \text{..... (6)}$$

The activation energies could be calculated from the plot of $\ln\sigma$ versus $1000/T$ according to equation (7).

$$\ln\sigma_{D.C} = \ln\sigma_0 - \frac{\Delta E_a}{kT} \quad \text{..... (7)}$$

Figure (6) show the variation of D.C conductivity (σ) vs. temperature (T), this figure show that (σ) increased with T, this is seems to be a normal behavior as one of semiconductor properties, due to the increasing carrier concentration with temperature. When ZnS added to the solution ($x=0.2, 0.4, \dots, 1$), $\sigma_{D.C}$ was decreased with increasing the ZnS Vol.% . The activation energy (E_a) obtained for these films is given in the table (2), which calculated from the slope of $\ln\sigma$ vs. $1000/T$ according to eq.(7) , which shown in Figure(7). From this figure the films having two activation energy depend on x value. This means there are two mechanisms for conductivity. The activation energy in the low temperature depends on the ionization impurity and at high temperature

depends on the generation of electron-hole pairs. Table(2) shows that the value of E_{a1} is smaller than values of E_{a2} . This indicates that the conductivity depends on the temperature where $\sigma \propto T^{3/2}$ [16].

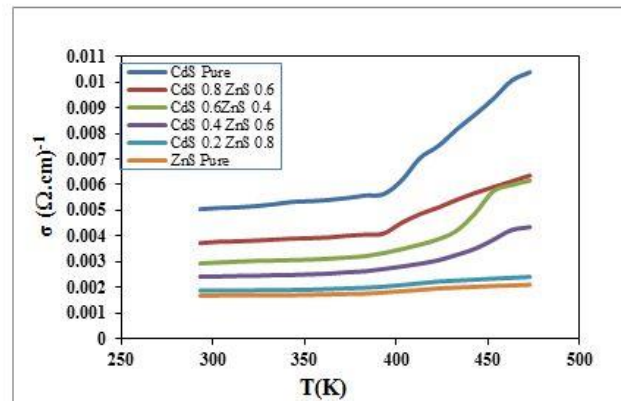


Figure (6): Variation of $\sigma_{D.C}$ versus temperature for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films at different Vol.% of (x).

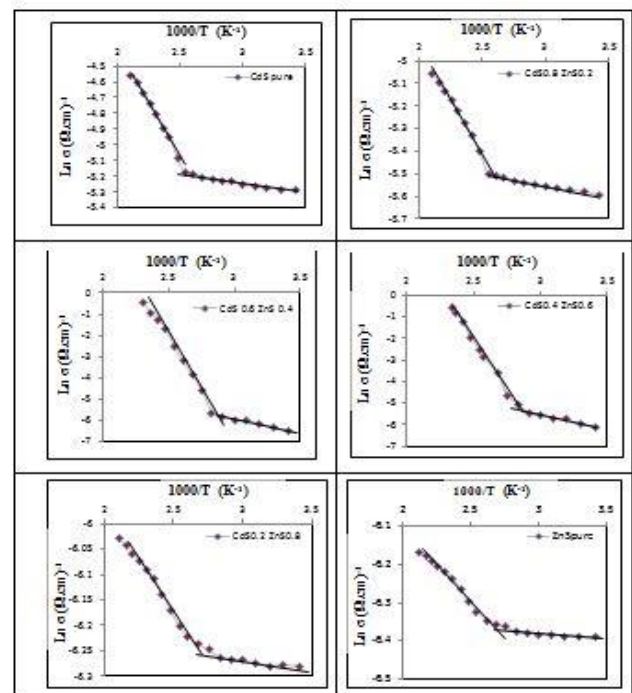


Figure (7) : $\ln\sigma$ versus $1000/T$ for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films at different Vol.% of (x).

Table 2: D.C. conductivity parameters for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ films at different Vol.% of (x).

Sample	E_{a1} (eV)	Temp.Rang e (K)	E_{a2} (eV)	Temp.Ra nge (K)	$\sigma_{R.T} \times 10^{-5}$ ($\Omega.cm$) ⁻¹
CdS pure	0.07473	(293-373)	0.1491	(373-473)	504
CdS _{0.8} ZnS 0.2	0.09182	(293-363)	0.1818	(363-473)	372
CdS _{0.6} ZnS 0.4	0.110398	(293-363)	0.2062	(353-473)	293
CdS _{0.4} ZnS 0.6	0.182459	(293-363)	0.2523	(383-473)	241
CdS _{0.2} ZnS 0.8	0.231569	(293-393)	0.3146	(383-473)	187
ZnS pure	0.281485	(293-393)	0.4058	(403-473)	167

The Hall effect system (HMS-3000) shown in Figure (8). Hall measurements of the deposited samples from $x = 0$ to $x = 1$ were shown p-type conductivity, which give positive values of R_H . The type of charge carriers, concentration (n_H), Hall mobility (μ_H), conductivity (σ) and resistivity (ρ) have been estimated from Hall measurements in the table (3).

From Table (3) the value of $\sigma_{R,T}$ was decreased with increasing of ZnS Vol.%. That the structure of thin film was changed to increase the grain size and increase barrier potential of the internal grains, which make capture to the change carriers in the grain bounding and then decrease the scattering. Mobility increases with increasing of ZnS Vol.%. is due to the decreasing of the carrier concentration.



Figure (8): set-up and Photograph illustrates the Hall Effect.

Table 3: The type of charge carriers, concentration (n_H), Hall mobility (μ_H), conductivity (σ) and resistivity (ρ) Cd_{1-x}Zn_xS films at different Vol.% of (x).

Sample	R_H (cm^2/C)	n_H ($1/\text{cm}^3$)	$\sigma_{R,T}$ ($\Omega.\text{cm}$) ⁻¹	$\rho_{R,T}$ ($\Omega.\text{cm}$)	μ_H (cm^2/Vs)
CdS _{pure}	2.487×10^6	2.510×10^{14}	9.643×10^6	1.089×10^2	1.213×10^2
CdS _{0.8} ZnS _{0.2}	6.358×10^6	9.817×10^{11}	8.589×10^6	1.171×10^2	5.088×10^2
CdS _{0.6} ZnS _{0.4}	9.349×10^6	6.677×10^{11}	8.002×10^6	1.250×10^2	6.210×10^2
CdS _{0.4} ZnS _{0.6}	1.717×10^7	3.635×10^{11}	5.775×10^6	1.794×10^2	9.160×10^2
CdS _{0.2} ZnS _{0.8}	7.178×10^6	8.697×10^{10}	5.334×10^6	1.875×10^2	6.128×10^2
ZnS _{pure}	8.084×10^6	7.722×10^{10}	4.875×10^6	2.051×10^2	7.424×10^2

IV. CONCLUSION

Cd_{1-x}Zn_xS mixed films were deposited on glass substrates at 360 °C and studied as a function of (x) Vol.%, $x(0 \leq x \leq 1)$. All samples exhibit low Absorbance less than 35% in the visible light spectrum. Refractive index approximately equal to a value of 2.5 and the absorption coefficients were in the range of 0.9 – 0.1 cm⁻¹ at wave length 500 nm. Energy gap of these films were found to be increasing with increasing in Vol.% of (x), while the photon transition was allowed direct transition, also Cd_{1-x}Zn_xS thin films had p-type, conductivity decrease with increasing of ZnS Vol % and had two activation energy. Mobility increase with increasing of ZnS Vol.%. $\sigma_{D,C}$ was decreased with increasing of ZnS Vol.%.

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